



POTENT SPECIFICATION

NO DRAWINGS

1,123,094

Date of Application and filing Complete Specification: 1 April, 1966.

No. 14480/66.

Application made in Czechoslovakia (No. 2191) on 2 April, 1965.

Complete Specification Published: 14 Aug., 1968.

© Crown Copyright 1968.

Index at acceptance:—C4 P(2G5A, 2H3, 2H5, 2H6, 2H11, 2H12, 2H13, 2H15, 2H21, 2HX, 9A3F); C2 J(1, 2)

Int. CL:—C 09 b 33/04

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are: BRETISSLAV BUDESINSKY, 16, Pakomericka 16, Prague 8, KAREL HAAS, 21, Zapotocni, Prague 10, Czechoslovakia, both citizens of Czechoslovakia.

COMPLETE SPECIFICATION

A process for the production of Substituted 2,7-Bis(Phenylazo) Derivatives of Chromotropic Acid

We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovakian body corporate of No. 3, Narodni, Prague, 1, Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of substituted 2,7-bis-(phenylazo) derivatives of chromotropic acid.

2,7-bis-(phenylazo) derivatives of chromotropic acid possess excellent metalochromic properties and are widely used as the most sensitive reagents for the determination of trace amounts of many metals, e.g. U, Pu, Np, Th, Zr, Hf, Ag, Cu, Ru, Pd, Ba, Ca, Mg, Nb, Y and lanthanides in aqueous media. Thus, 0.01 μ g of the corresponding metal per 1 ml of the solution can be determined by means of the above reagents. In some cases, these reagents can be used as indicators in complexometric titrations. The preparation of 2,7-bisphenylazo derivatives of chromotropic acid requires, however, the fulfilment of many conditions.

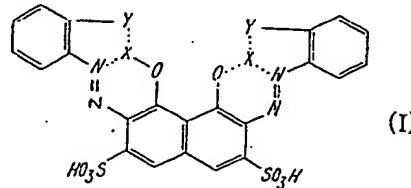
Removal of a proton from the phenolic hydroxylic function is a known condition for coupling of phenols with diazonium salts. Chromotropic acid which possesses two phenolic hydroxylic functions loses the proton of the second function ($pK 15.6$) with extreme difficulty because of the formation of hydrogen bondings. This fact renders the preparation of chromotropic acid 2,7-bis-(phenylazo) derivatives rather difficult. To a certain degree, formation of these derivatives may be facilitated by the presence of Ca^{2+} ions, as shown by Kuznecov.

We have found that removal of the proton

from the second phenolic hydroxylic function of chromotropic acid can be advantageously accomplished by a simultaneous nucleophilic action of organic bases as well as ions of certain alkaline earth metals (Be, Mg, Ca, Sr) at a pH of 10—14. The action of the aforementioned ions consists in the formation of chelate complexes with both phenolic hydroxylic functions.

Our investigations on the 2,7-bis-(phenylazo) derivatives of chromotropic acid have shown that to the bathochromic forms of derivatives possessing the $-\text{OH}$, $-\text{SH}$, $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{SeO}_2\text{H}$, $-\text{AsO}_3\text{H}_2$, $-\text{PO}_3\text{H}_2$, $-\text{SbO}_3\text{H}_2$, $-\text{BO}_2\text{H}_2$ or $-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$

groups in the ortho position of the benzene ring in respect to the azo group, the symmetrical structure I can be ascribed



wherein Y represents $-\text{O}^-$, $-\text{S}^-$, $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{SeO}_2^-$, $-\text{AsO}_3\text{H}^-$, $-\text{PO}_3\text{H}^-$, $-\text{SbO}_3\text{H}^-$, $-\text{BO}_2\text{H}^-$ or $-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$, and X is a hydrogen atom (H) or a cation of a metal (M).

The occurrence of this structure can be utilised for a test of the formation of the 2,7-bis-(phenylazo) derivatives. The "bisazo test" is performed by adding 1 drop of the reaction mixture into 2—5 ml of concentrated

[Price 4s. 6d.]

45

50

55

60

65

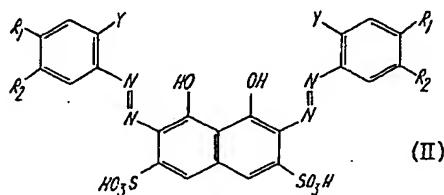
70

75

D7

sulfuric acid: an intensive green color (absorption maximum at 640—660 m μ) appears in the presence of a bisazo dye, whereas the monoazo derivatives produce a blue color (absorption maximum at 600—610 m μ).

5 The metalochromic selectivity and sensitivity of chromotropic acid 2,7-bis-(phenylazo) derivatives of the general formula I (see above) may be increased by introduction of additional groups (R₁, R₂, and where R₁ may be the same as R₂ if desired) into the benzenic moiety, which groups influence the acidity of the donor groups located in the ortho position to the azo group. The structure of the resulting derivatives is shown in the general formula II:—



wherein Y represents an —OH, —SH, —COOH, —SO₃H, —SeO₂H, —AsO₃H₂, —PO₃H₂, —SbO₃H₂, —BO₃H₂ or a 20 —CH₂N(CH₂COOH)₂ group, and R₁ and R₂ may be the same or different, and each is —H, —COOH, —SO₃H, —NO₂, —NHCOCH₃, —N(CH₃)₂, —N(C₂H₅)₂, —CH₃, —Cl, —Br or —F. The most remarkable effect is encountered 25 when a carboxylic function, a sulfonic acid residue or a nitro group are introduced.

The preparation of the required diazonium salt of formula R₁, R₂, YC₆H₄N₂A, where 30 A is the chloride or sulphate anion and wherein the symbols Y, R₁, and R₂ represent the same as in formula II above, can be performed in the usual manner by diazo- 35 tisation of the corresponding aniline derivative with sodium nitrite in dilute hydrochloric acid or, in the case of nitro or carboxy derivatives, in concentrated sulfuric acid. Moreover, a consider- 40 able excess of the diazonium salt is necessary (in addition to an efficient stirring and a suitable temperature) to convert chromotropic acid or its 2-monoazo derivative into the corresponding 2,7-bisazo dye. The reac- 45 tion is preferably carried out as follows. Both components, the solution of the diazonium salt and the solution of chromotropic acid are added dropwise at pH 10—14 into a saturated solution of the alkaline earth metal ions (Be, Mg, Ca, Sr) in a 1:1 to 1:5 50 solution of an organic base in water, e.g. a quaternary ammonium hydroxide (such as tetramethylammonium hydroxide), an aliphatic tertiary amine such as trimethylamine, pyridine, or quinoline. When a monoazo 55 derivative of chromotropic acid is used as

the starting material, it has to be previously dissolved in a 1:1 to 1:5 solution of the aforementioned organic bases in water. The necessary amount of the diazonium salt is determined by the above "bisazo test". A two-fold to five-fold excess of the diazonium salt in contrast to the theoretical amount is usually necessary for the formation of a 2,7-bisazo dye.

60 The alkaline earth metal (Be, Mg, Ca, and Sr) may be used in the form of their oxides or hydroxides. These may be prepared as extremely fine suspensions or by precipitation of the corresponding salts with alkali hydroxides in an aqueous medium.

65 The course of the coupling reaction is highly influenced by temperature and the rate of addition of both components. The temperature of the diazonium salt solution and of the coupling mixture should be below 0°C. and preferably should lie in the range between —5° and —3°C. Both components should be added very slowly thus, the preparation of about 0.01 mole of the 2,7-bisazo 70 dye should require approximately 30 minutes. When the temperature and kinetic conditions are not adhered to a considerable decomposition of the diazonium salt occurs (frothing) leading to very low yields of the 2,7-bisazo 75 dye.

80 In contrast to the rapid and almost quantitative formation of the 2-monoazo dye, the 2,7-bisazo dye requires longer periods of time and a considerable excess of the diazonium salt; to prevent decomposition of the diazonium salt, lower temperatures should be applied which, however, decrease the rate of the reaction. A compromise between these requirements is therefore necessary. When 85 the addition of the components is finished, the reaction mixture is allowed to stand at the aforementioned temperature for 30 to 120 minutes in view of the slow rate of coupling 90 reaction.

95 The 2,7-bisazo dye is precipitated by acidification of the solution with hydrochloric acid; preferably the temperature should not exceed 0°C. In some cases, especially in the case of phosphonic and arsionic derivatives, a 20—40% hydrochloric acid is necessary to break the unusually stable complexes with the alkaline earth metals. Under these conditions, the precipitation is almost quantitative; two to five reprecipitations under normal temperature, are however, necessary to remove the last traces of the alkaline earth metals (purest hydrochloric acid and redistilled water are required). The alkaline earth metals can be removed also by passage through ion exchange 100 resins but a considerable amount of the dye is lost by this procedure.

105 The following examples serve to further illustrate the present invention. Because of simplicity, abbreviations are used for naming the bisazo dyes.

60

65

70

75

80

85

90

95

100

105

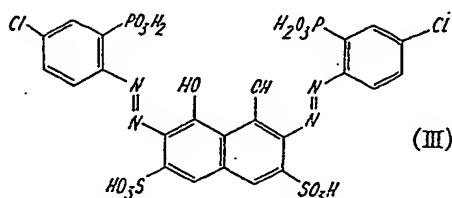
110

115

120

EXAMPLE 1.

The DI-(CHLOROPHOSPHONAZO) compound (cf. Formula III).



5 A suspension of finely ground 2-amino-5-chlorophenylphosphonic acid (6.2 g; 0.03 mole) in water (20 ml) and concentrated hydrochloric acid (5 ml) is cooled to -5°C and diazotised with a solution of sodium nitrite (2.1 g) in water (10 ml) at a temperature not exceeding -3°C . A solution of chromotropic acid (3.65 g; 0.01 mole) in water (20 ml) and pyridine (5 ml) is then prepared; approx. 5 ml of the resulting solution is added into a suspension of finely ground calcium oxide (4.0 g) in water (20 ml) and pyridine (5 ml), the whole is cooled to -5°C and treated dropwise (with the rate 0.5 drop per sec) under efficient stirring with the above diazonium salt solution (cooled to -5°C to -3°C) till a sample of the reaction mixture (1 drop) shows a grass-green color (a positive bisazo test) on treatment with 3—5 ml of concentrated sulfuric acid. As soon as the bisazo test is positive, additional portions of the above solution of chromotropic acid are added dropwise (0.5 drop per sec.) simultaneously with the diazonium salt solution. The bisazo test is repeated every time after the addition of a 5 ml portion of the chromotropic acid solution. When the test is negative the addition of the chromotropic acid solution is stopped and only the addition of the diazonium salt solution is continued till the bisazo test is positive again. The two solutions are then added simultaneously and the reaction is controlled in the same manner as above until all the diazonium salt solution is consumed. The reaction mixture is then stirred at -5° to -3°C for an additional 30—60 minutes. After acidification with 50 ml of concentrated hydrochloric acid at a temperature not exceeding 0°C , the mixture is kept overnight in a refrigerator and collected with suction. The precipitate is washed with 20 ml of dilute (1:1) hydrochloric acid previously cooled to 0°C and dried at 105°C for 3 hours to remove the main portion of hydrochloric acid. The dried precipitate is dissolved in 20 ml of 1M sodium hydroxide, the solution is filtered, the filtrate is added dropwise into 30 ml of concentrated hydrochloric acid, the mixture is stored for 3 hours in a refrigerator and worked up as above. The

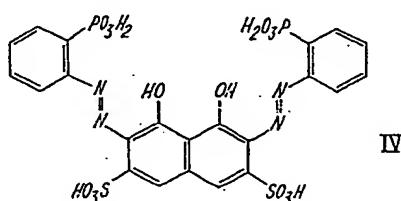
reprecipitation is repeated three times with the use of purest concentrated hydrochloric acid, distilled water and purest sodium hydroxide entirely free of calcium ions (because of the highly stable alkaline earth metals complexes formed—see above). The precipitate is finally dried at 105°C for 12 hours to afford approximately 3.5 g (46%) of the DI-(CHLOROPHOSPHONAZO) compound (cf. Formula III). Its $2.00 \cdot 10^{-5}\text{M}$ solution gives at pH 6.5—7.0 with Ca^{2+} ions the most sensitive reaction (molar extinction coefficient approximately $40,000 \text{ cm}^2 \text{ mmole}^{-1}$ at the wave length 660 nm).

60

65

70

EXAMPLE 2.
The DI-(PHOSPHONAZO) compound (cf. Formula IV).



A. Preparation of o-aminophenylphosphonic acid. A suspension of finely ground calcium carbonate (5 g) in water (50 ml) is treated dropwise under stirring with a 5% aqueous solution of palladium chloride and the mixture is adjusted with 1N sodium hydroxide to pH 8—10. The precipitate is collected with suction and dried at 105°C . The resulting catalyst is added to a solution of 2-amino-5-chlorophenylphosphonic acid (6.2 g; 0.03 mole) in 1N sodium hydroxide (60 ml) and 96% ethanol (80 ml), and the mixture is hydrogenated at room temperature and ordinary pressure until the hydrogen uptake is 670—720 ml. The catalyst is then filtered off and the filtrate is evaporated under reduced pressure to remove the ethanol completely. The residue contains about 0.03 mole of o-aminophenylphosphonic acid and is used directly in the next step.

75

80

85

90

95

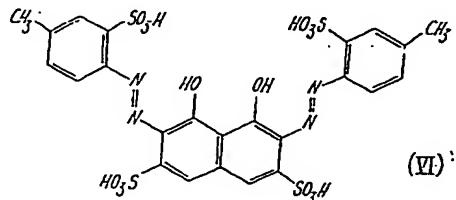
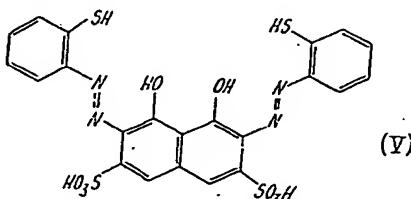
100

B. Preparation of the DI-(PHOSPHONAZO) compound (cf. Formula IV). o-Aminophenylphosphonic acid prepared according to the preceding paragraph (approximately 0.03 mole) is dissolved in water (20 ml) and concentrated hydrochloric acid (5 ml), and the solution is worked up analogously to EXAMPLE

1. Yield, approximately 3 g (44%) of the DI-(PHOSPHONAZO) compound which has not been hitherto described in the literature and which represents an excellent reagent for the spectrophotometric determination of uranium, thorium, lanthanides and yttrium.

105

EXAMPLE 3.
The DI-(MERCAPTOAZO) compound (cf. Formula V).



A. Preparation of o-aminophenyl xanthogenate. A mixture of sodium hydroxide (2.4 g; 0.06 mole), 96% ethanol (50 ml) and carbon disulfide (4.6 g; 0.06 mole) is treated with o-bromonitrobenzene (8.1 g; 0.04 mole) and the whole is refluxed for 1.5 to 2 hours. The ethanol is removed by evaporation under reduced pressure and the residue is extracted with four 30 ml portions of ether. The ethereal extracts (containing the principal portion of o-nitro-phenyl xanthogenate) are evaporated and the residue is refluxed with 1000 ml of glacial acetic acid and 60 g of zinc dust for one hour. The excess zinc is filtered off and the filtrate is evaporated to dryness under reduced pressure. The residue represents approximately 0.06 mole of o-aminophenyl xanthogenate which may be directly used in the next step.

B. Preparation of the DI-(MERCAPTOAZO) compound (see Formula V). A solution of approximately 0.06 mole of o-aminophenyl xanthogenate in water (40 ml) and concentrated hydrochloric acid (5 ml) is worked up analogously to Example 1 to afford approximately 5 g (65%) of the DI-(XANTHOGENOAZO) compound which is converted to the dimercapto azo compound by refluxing with 1000 ml of 20% aqueous hydrochloric acid for two hours and evaporation under reduced pressure. The crude product is dissolved in 1N sodium hydroxide (50 ml), the solution filtered and the filtrate precipitated with 10 ml of concentrated hydrochloric acid to give approximately 3.2 g (54%) of the DI-(MERCAPTOAZO) compound.

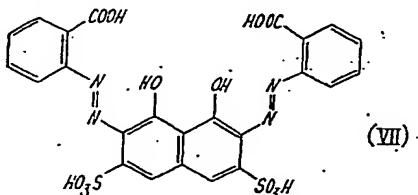
Instead of carbon disulfide, an equivalent amount of thioacetic acid may be used to obtain o-aminophenyl thioacetate and finally the DI-(THIOACETYLATO) compound which affords by hydrolysis in the analogous manner as above the DI-(MERCAPTOAZO) compound. This dye has not been hitherto described in the literature. The DI-(MERCAPTOAZO) compound represents an excellent spectrophotometrical reagent for the determination of thorium, uranium and some other elements.

EXAMPLE 4.
The DI-(METHYLSULFONAZO) compound (cf. Formula VI).

A solution of p-toluidine-m-sulfonic acid (7.5 g; 0.04 mole) in 50 ml of 1N sodium hydroxide (the solution must show a distinct alkaline reaction) is treated with sodium nitrite (2.8 g), cooled to 0°C, and the whole is added at max. 0°C into a precooled (-5°C) solution of concentrated hydrochloric acid (10 ml) in water (10 ml). The resulting suspension of the diazonium salt is added dropwise at max. 0°C into a mixture prepared previously by treatment (at -5°C) of a solution of chromotropic acid (3.65 g; 0.01 mole), water (20 ml) and pyridine (5 ml) under stirring and cooling to -5°C with finely ground calcium oxide (3 g). The course of the coupling is controlled by means of the bisazo test. In this case the grass-green color sometimes does not appear after the addition of the total amount of the diazonium salt solution. Notwithstanding, the reaction mixture does contain the bisazo dye and is worked up as follows. The reaction mixture is allowed to stand at max. 0°C for 20-30 minutes, acidified at max. 0°C with concentrated hydrochloric acid (20 ml) and stored in a refrigerator overnight. The precipitate is collected with suction, dried at 105°C for 6-12 hours and dissolved in 1N sodium hydroxide (50 ml). The solution is precipitated with concentrated hydrochloric acid, allowed to stand overnight, filtered, the precipitate washed with 5-10 ml of cooled 5% aqueous hydrochloric acid and dried at 105°C for 6-12 hours. The resulting DI-(METHYLSULFONAZO) compound has not been hitherto described in the literature. The dye represents the most sensitive reagent for the spectrophotometric determination of strontium and barium. Yield, ca 2.2 g (30%).

EXAMPLE 5.

The DI-(CARBOXYAZO) compound (cf. Formula VIII).



A solution of anthranilic acid (5.48 g; 0.04 mole) in water (40 ml) and concentrated hydro-

55

60

65

70

75

80

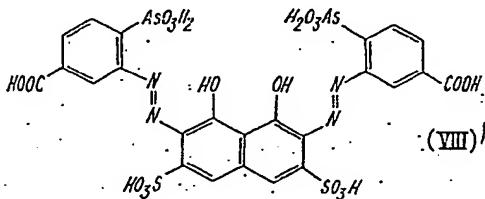
85

90

95

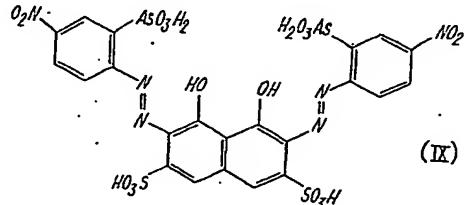
chloric acid (5 ml) is cooled to -5°C and diazotised under stirring at max. 0°C with sodium nitrite (2.8 g) in water (10 ml). The resulting solution of the diazonium salt is then added dropwise under stirring at max. 0°C into a solution of chromotropic acid (3.65 g; 0.01 mole) in 50 ml of 5M aqueous trimethylamine or tetramethylammonium hydroxide pretreated with 5 g of finely ground magnesium hydroxide and precooled to -5°C . The course of the reaction is controlled by means of the bisazo test. The final reaction mixture is stored at max. 0°C for 60 minutes, acidified under stirring at a temperature not exceeding 0°C with concentrated hydrochloric acid (50 ml) and worked up analogously to Example 4 to afford approximately 2 g of the DI-(CARBOXYAZO) compound which has not been hitherto described in the literature and which represents an excellent reagent for the determination of thorium, uranium and lanthanides.

EXAMPLE 6.
The DI-(CARBOXYARSONAZO) compound (cf. Formula VIII).



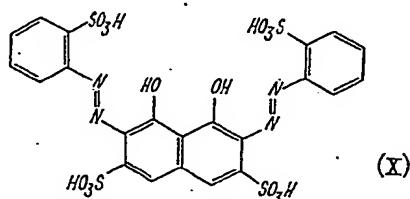
A suspension of finely ground 2-amino-4-carboxyphenylarsonic acid (10.5 g; 0.04 mole) in water (20 ml) and concentrated hydrochloric acid (5 ml) is cooled to -3°C and diazotised under cooling at a temperature not exceeding -3°C with a solution of sodium nitrite (2.8 g) in water (10 ml). The mixture is then worked up analogously to Example 1. Approximately three reprecipitations are performed with the use of about 20 ml 1N sodium hydroxide and 10 ml concentrated hydrochloric acid. The collected precipitate can be used directly for the next reprecipitation (drying of the precipitate is not necessary). Yield 3.8 g (44%) of the di-(carboxyarsonaze) compound, the best reagent hitherto known for the spectrophotometric determination of rare earths.

EXAMPLE 7.
The DI-(NITROARSONAZO) compound (cf. Formula IX).



Finely ground 2-amino-5-nitrophenylarsonic acid (10.5 g; 0.04 mole) is diazotised, coupled with chromotropic acid and the resulting product purified analogously to Example 6 to afford 3.2 g (37%) of the DI-(NITROARSONAZO) compound which has not been hitherto described and which represents an excellent reagent for the spectrophotometrical determination of rare earths.

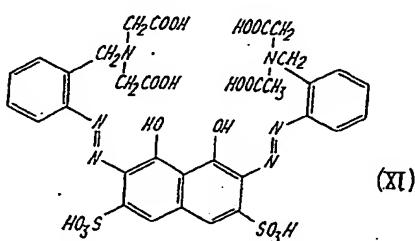
EXAMPLE 8.
The DI-(SULFONAZO) compound (cf. Formula X).



Aniline-o-sulfonic acid (5.2 g; 0.04 mole) is dissolved in 1N sodium hydroxide (35 ml), the solution is cooled, treated with 2.1 g of sodium nitrite in 10 ml of water and the whole is added dropwise under stirring at a temperature not exceeding -3°C into 15 ml of dilute (1:1) hydrochloric acid precooled to -3°C . The resulting suspension of the diazonium salt is added portionwise at max. -3°C into a mixture (precooled to -5°C) previously prepared by suspending 4 g of extremely finely ground calcium oxide in a solution of chromotropic acid dihydrate (3.56 g; 0.01 mole), water (20 ml) and pyridine (5 ml). The bisazo test is carried out after the addition of every 1/5 (vol.) of the diazonium salt solution. The above stated amount of the diazonium salt is usually quite sufficient (in some runs even slightly superfluous) for a successful conversion of the total chromotropic acid into the bisazo dyestuff. The stirring and cooling of the reaction mixture is continued for 30—60 minutes. The mixture is then acidified at max. 0°C . with 25 ml of concentrated hydrochloric acid, stored in a refrigerator overnight and filtered off. The precipitate is dissolved in 1N sodium

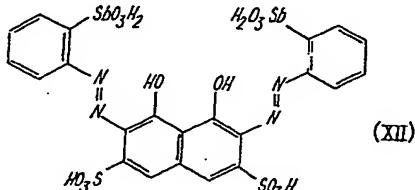
hydroxide (20 ml), the solution filtered and the filtrate acidified with 10 ml of concentrated hydrochloric acid. This purification procedure is repeated once more. Yield, 2.1 g (27%) of the DI-(SULFONAZO) compound. Free evaporation and reprecipitation affords additional 1 g of the dyestuff. The DI-(SULFONAZO) compound represents a sensitive and selective reagent for the determination of Ba^{2+} ions. Its $2.00 \cdot 10^{-5}$ M solution shows at pH 2.4 and wave length of 665 nm the molar extinction coefficient 11 800 $cm^2 \text{ mmole}^{-1}$.

EXAMPLE 9
15 The DI-(AMINOMETHYLAZO) compound (cf. Formula XI).



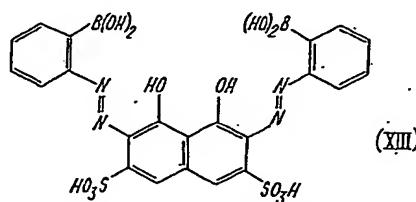
20 A mixture of o-aminobenzyliminodiacetic acid (9.0 g; 0.04 mole) and water (50 ml) is acidified with hydrochloric acid (10 ml), cooled to -3°C and worked up analogously to Example 6 (6 g of finely ground calcium oxide is used in the present preparation instead of 4 g given in Example 6). Yield, 25 4.2 g (51%) of the DI-(AMINOMETHYL-AZO) dye. In the case of Cu^{2+} ions, its $2.00 \cdot 10^{-5}$ M solution shows at pH 10.5—2.0 11.0 and at the wavelength of 600 nm the molar extinction coefficient 85 000 $cm^2 \text{ mmole}^{-1}$.

EXAMPLE 10.
The DI-(STIBONAZO) compound (cf. Formula XIII).



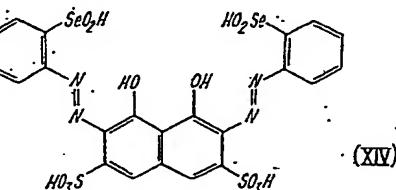
35 Finely ground o-aminophenylstibonic acid (10.56 g; 0.04 mole) is worked up analogously to Example 6 to afford 4.1 g (47%) of the distibonazo compound which represents a sensitive reagent for the determination of thorium.

EXAMPLE 11.
The DI(BORONAZO) compound (cf. Formula XIII).



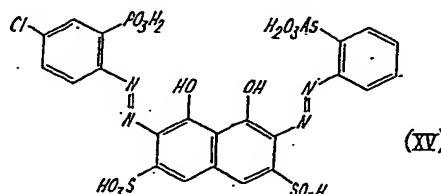
45 Finely ground o-aminophenylboronic acid (5.5 g; 0.04 mole) is worked up in analogy to EXAMPLE 6 to afford approximately 3.2 g (52%) of the DI(BORONAZO) compound which has not been hitherto described in the literature and which represents a very sensitive reagent for the determination of thorium.

EXAMPLE 12.
The DI(SELENAZO) compound (see Formula XIV).



55 o-aminophenylseleninic (7.1 g; 0.03 mole) is worked up in analogy to EXAMPLE 8. Yield, 3.5 g (39%) of the DI(SELENAZO) compound which has not been described hitherto in the literature and which represents a sensitive reagent for the determination of copper and lanthanides.

EXAMPLE 13.
The CHLOROPHOSPHONAZOARSON-AZO compound (cf. Formula XV).



70 A suspension of finely ground 2-amino-5-chlorophenylphosphonic acid (4.1 g; 0.02 mole) in water (20 ml) and concentrated hydrochloric acid (5 ml) is cooled to -5°C and diazotised under stirring at max. -3°C with a solution of sodium nitrite (1.4 g) in 7 ml of water (component A). A solution of 2-(o-arsonophenylazo)-chromotropic acid in water (20 ml) and 5 ml of pyridine (component B) and a suspension (precooled to -5°C) of extremely finely ground calcium oxide (4 g) in water (20 ml) and 5 ml of pyridine (com-

50

55

60

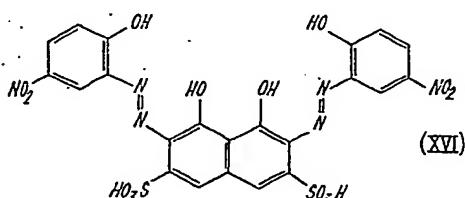
65

70

75

ponent C) are then prepared. Components A, B and C are worked up in analogy to EXAMPLE 1. Yield, 4.5 g (57%) of the CHLOROPHOSPHONAZOARSONAZO 5 compound which represents an excellent spectrophotometrical reagent for the determination of uranium and rare earths.

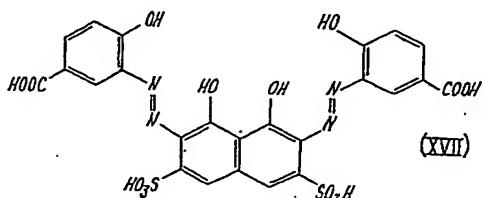
EXAMPLE 14.
The DI-(NITROHYDROXYAZO) compound (cf. Formula XVI).



Dried and finely ground sodium nitrite is added portionwise under stirring into concentrated sulfuric acid the temperature being kept below +10°C. The solution should be colorless and no nitrous gases should evolve. The solution is then placed into a cold water bath and stirring is continued. As soon as the solution reaches the temperature of the water bath, it is heated gradually to 70°C to dissolve the residual sodium nitrite (the reaction mixture should be colorless and no nitrous gases should evolve). The solution is then cooled to 20°C and treated portionwise under stirring with finely ground p-nitro-o-aminophenol (4.6 g; 0.03 mole). Stirring is continued for 10 minutes at room temperature, the mixture is poured onto 73 g of crushed ice and the insoluble solid is removed by filtration. The filtrate (component A), a suspension of finely ground calcium oxide (16.3 g) in 50 ml of water and 5 ml of pyridine (component B) and a solution of chromotropic acid (3.65 g; 0.01 mole) in 20 ml of water and 5 ml of pyridine (component C) are then worked up in analogy to EXAMPLE 1.

In the first purification with 20 ml of 1M sodium hydroxide a considerable amount of material does not dissolve (predominantly calcium sulfate). Yield, approximately 2 g (31%) of the DI(NITROHYDROXYAZO) compound which has not been described hitherto in the literature and which represents an excellent reagent for the determination of ruthenium, silver, copper, palladium and sodium.

EXAMPLE 15.
The DI(CARBOXYHYDROXYAZO) compound (cf. Formula XVII).

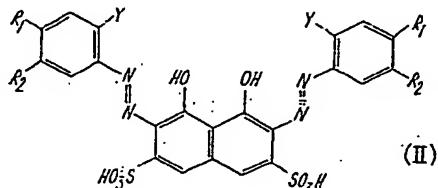


A suspension of finely ground o-amino-p-carboxyphenol (5.1 g; 0.04 mole), water (20 ml) and concentrated hydrochloric acid (5 ml) is worked up in analogy to EXAMPLE 6 to afford 3.5 g (57%) of the DI(CARBOXYHYDROXYAZO) compound which has not been described hitherto in the literature and which represents an excellent reagent for the determination of thorium.

Note: The following nomenclature has been used in the specification: —PhSeO₂H phenylseleninic acid, PhB(OH)₂ phenylboronic acid, PhPO₃H₂ phenylphosphonic acid, PhAsO₃H₂ phenylarsonic acid, and PhSbO₃H₂ phenylstibonic acid.

WHAT WE CLAIM IS:—

1. A process for the production of substituted 2,7-bis-phenylazo derivatives of chromotropic acid of the general formula:—



wherein Y represents an —OH, —SH, —COOH, —SO₃H, —SeO₂H, —AsO₃H₂, —PO₃H₂, —SbO₃H₂, —B(OH)₂, or —CH₂N(CH₂COOH)₂,

group and R₁ and R₂ which may be the same or different, represent hydrogen, —COOH, —SO₃H, —NO₂, —NHCOCH₃, —N(CH₃)₂, —N(C₂H₅)₂, —CH₃, —Cl, —Br or —F, which process comprises coupling the diazonium salts of the general formula

R₁ R₂ YC₆H₄N₂A,

where A is the chloride or sulphate anion, and wherein the symbols Y, R₁ and R₂ represent the same as in the general formula II, under stirring at a temperature below 0°C in an aqueous alkaline medium at pH 10—14 and in the presence of organic bases and ions of the alkaline earth metals Be, Mg, Ca and Sr, with chromotropic acid to form the corresponding bisazo derivatives and purifying the latter by precipitation with hydrochloric acid to remove the metal ions.

2. A process according to claim 1, wherein

55

60

65

75

80

85

90

pyridine, quinoline, trimethylamine, tetra-methylammonium hydroxide are used as organic bases in the ratio 1:1 to 1:5 to water.

5 3. A process according to claim 1, wherein Be, Mg, Ca and Sr are used as oxides or hydroxides, in the form of extremely fine suspensions or may be prepared by precipitation of the corresponding salts with alkali hydroxides in an aqueous medium.

10 4. A process according to claim 1, wherein the —SH group of the coupling component is protected in the form of —S—CS—OR or —S—COCH₃, and the free —SH group is obtained by final acid hydrolysis.

15 5. A process according to claim 1, wherein the coupling temperature is advantageously kept between 0° and -5°C.

20 6. A process according to claim 1, wherein the course of the coupling reaction is monitored by adding a sample of the coupling reaction mixture (1 drop) into concentrated sulfuric acid (5 ml) whereby the formation of a bisazo dye is shown by a characteristic grass-green color whereas the monoazo compounds give a blue color.

25 7. A process for the production of substituted 2,7-bis(phenylazo) derivatives of chromotropic acid according to any one of the Examples.

30 8. 2,7-Bis(phenylazo) derivatives of chromotropic acid, prepared according to any one of the methods of claims 1 to 7 as highly sensitive metalochromic reagents for the spectrophotometrical determination of metals.

35

H. D. FITZPATRICK & CO.,
Chartered Patent Agents,
5, Park Gardens,
Glasgow, C.3
and 27, Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.